

INTERDIFFUSION OF HgTe/CdTe HETERO-INTERFACES

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H.G. Robinson and S.L. Gleixner
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

W.J. Hamilton, J.L. Johnson, and K. Kosai
Raytheon IR Center of Excellence
75 Coromar Drive
Goleta, CA, 93117

ABSTRACT

In this paper we present results of a study of interdiffusion in HgTe/CdTe heterostructures. Our samples were grown by MBE at HRL Laboratories and had Cd x values ranging from 0.2 to 0.35. The samples were annealed at temperatures ranging from 250 °C to 425 °C in both Hg vapor and vacuum ambients. The samples annealed under vacuum were coated with a layer of CdTe prior to annealing. The data were simulated using Darken's equation, and results show strong agreement between the simulated and experimental profiles. Significantly more diffusion was observed for anneals under Hg-rich ambients than under vacuum. For Hg-rich anneals, the activation energy was 1.50 eV at temperatures less than 350 °C and 1.33 eV at higher temperatures. This is the first time that two activation energies for the interdiffusion coefficient have been reported. The mechanisms responsible for this behavior are discussed.

1.0 INTRODUCTION

The fabrication of all HgCdTe-based infrared detectors involves the formation of one or more hetero-interfaces. With the increasing interest in developing detectors in the SWIR as well as the MWIR and LWIR bands, and the desire for multispectral sensitivity, the number and complexity of hetero-interfaces is increasing. Because the performance of these detectors depends critically on the precise placement of the hetero-interfaces, any interdiffusion at these interfaces must be understood and controlled. Although much work has been done in this area, the mechanisms underlying the diffusion are still not fully understood [1-5]. Moreover, a comprehensive model of the interdiffusion that accounts for variations in temperature, Hg pressure, x value, and Fermi level has not been developed. Recent advances

in process modeling codes now make it possible to build a numerical model of interdiffusion that accounts for the above dependencies [6, 7].

Interdiffusion is usually modeled using a form of Darken's equation [8]:

$$D_{MCT} = [D_{Cd}(1-x) + D_{Hg}x] \left[1 + \frac{\partial \ln \gamma_{Cd}}{\partial \ln x} \right] \quad (1)$$

Here D_{Cd} is the diffusion of Cd in HgTe, D_{Hg} the diffusion of Hg in CdTe, x the Cd fraction, and γ the activity coefficient. The second term in brackets is known as the thermodynamic factor. The thermodynamic factor accounts for the fact that the diffusivity depends nonlinearly on x . When γ equals zero, the interdiffusion coefficient is linear with x and the system is said to be ideal. γ is a measure of the chemical potential of the system. In binary alloys, it is a function of x value, temperature, and any other influences on the chemical potential, such as the position of the Fermi level. For pseudobinary alloys, such as HgCdTe, the anion-to-cation stoichiometry must also be accounted for. This usually takes the form of the partial pressure of the dominant vapor species (Hg in the case of HgCdTe). Modeling interdiffusion is therefore a matter of defining the activity coefficient as a function of the critical variables. For HgCdTe, these are x value, Hg pressure, temperature, and Fermi level.

Although Darken's equation is physically correct, it does not tell us anything about the atomic-level mechanisms controlling the diffusion. If the atomic mechanisms are understood and accurately calibrated, then the activity coefficient as a function of the critical variables can be determined. Diffusion in semiconductors occurs via point defects. In the case of HgCdTe, the dominant defects for diffusion are cation vacancies and interstitials. These species may be electrically charged, but the location of the energy levels is not accurately known. Diffusion via charged point defects means that Fermi level effects are particularly important in HgTe/CdTe interdiffusion because of the strong dependence of the band gap on x value. The full set of coupled continuity equations can be written as [9]:

$$\begin{aligned} \frac{\partial C_{Hg_{cation}}}{\partial t} = \nabla \left\{ \frac{D_v}{C_{cation}} (C_v \nabla C_{Hg_{cation}} - C_{Hg_{cation}} \nabla C_v) \right\} - g_{Hg} C_{Hg_{cation}} (j-k)n \\ + k_{R_{Hg}} C_{Hg_I} C_v + k_{KOHg} C_{Hg_I} C_{Cd_{cation}} (l-k)n - k_{KOCd} C_{Cd_I} C_{Hg_{cation}} \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial C_v}{\partial t} = \nabla (D_v \nabla C_v) + \frac{jq}{kT} \nabla (D_v C_v \nabla \Psi) \\ + g_{Hg} C_{Hg_{cation}} (j-k)n - k_{R_{Hg}} C_{Hg_I} C_v + g_{Cd} C_{Cd_{cation}} (j-l)n - k_{R_{Cd}} C_{Cd_I} C_v \end{aligned} \quad (3)$$

$$\frac{\partial C_{Cd_{cation}}}{\partial t} = - \left(\frac{\partial C_v}{\partial t} + \frac{\partial C_{Hg_{cation}}}{\partial t} \right) \quad (4)$$

$$\begin{aligned} \frac{\partial C_{\text{HgI}}}{\partial t} = & \nabla (D_{\text{HgI}} \nabla C_{\text{HgI}}) - \frac{kq}{kT} \nabla (D_{\text{HgI}} C_{\text{HgI}} \nabla \Psi) \\ & + g_{\text{Hg}} C_{\text{Hg}_{\text{cation}}} (j-k)n - k_{\text{RHg}} C_{\text{HgI}} C_{\text{V}} - k_{\text{KOHg}} C_{\text{HgI}} C_{\text{Cd}_{\text{cation}}} (l-k)n + k_{\text{KOCd}} C_{\text{CdI}} C_{\text{Hg}_{\text{cation}}} \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{\partial C_{\text{CdI}}}{\partial t} = & \nabla (D_{\text{CdI}} \nabla C_{\text{CdI}}) - \frac{lq}{kT} \nabla (D_{\text{CdI}} C_{\text{CdI}} \nabla \Psi) \\ & + g_{\text{Cd}} C_{\text{Cd}_{\text{cation}}} (j-l)n - k_{\text{RCd}} C_{\text{CdI}} C_{\text{V}} + k_{\text{KOHg}} C_{\text{HgI}} C_{\text{Cd}_{\text{cation}}} (l-k)n - k_{\text{KOCd}} C_{\text{CdI}} C_{\text{Hg}_{\text{cation}}} \end{aligned} \quad (6)$$

D_{HgI} and D_{CdI} are the diffusion coefficients for Hg and Cd interstitials. D_{V} , the vacancy diffusion coefficient, is a combination of vacancies diffusing by exchanging with Hg atoms, D_{V}^{Hg} , and those diffusing by exchanging with Cd atoms, D_{V}^{Cd} , where $D_{\text{V}} = (1-x_{\text{Cd}})D_{\text{V}}^{\text{Hg}} + x_{\text{Cd}}D_{\text{V}}^{\text{Cd}}$. $C_{\text{HgI}}^{\text{equil}}$, $C_{\text{CdI}}^{\text{equil}}$, and $C_{\text{V}}^{\text{equil}}$ are the equilibrium Hg and Cd interstitial concentrations and equilibrium cation vacancy concentration. $C_{\text{Hg}_{\text{cation}}}$, $C_{\text{Cd}_{\text{cation}}}$, C_{cation} are the concentrations of Hg, Cd, and total cation sites. n is the concentration of free electrons and q is the charge of an electron. Ψ is an electric field created by either an externally applied potential, internal variations in the bandgap, or charged point defect concentrations.

Elucidating the parameters for the atomic mechanisms requires a combination of careful experimental study and first principals, *ab-initio* modeling. Toward this end, we have conducted an experimental study of interdiffusion in undoped HgCdTe at Cd compositions between 0.2 and 0.35. The results of this study are presented below. Much work remains to be done before a comprehensive model is obtained that can simulate interdiffusion in HgCdTe as a function of all the critical variables. However, these data provide a good foundation on which to build such a model.

2.0 EXPERIMENTAL PROCEDURE

The samples used in the study were grown by MBE at HRL Laboratories on CdZnTe substrates. Two types of samples were grown: a single step in x value from 0.2 to 0.25 to 0.2, and three steps in x value – 0.2, 0.25, 0.2, 0.3, 0.2, 0.35, 0.2. The samples were annealed at temperatures ranging from 275°C to 425°C. The annealing times at each temperature were set by simulating the expected interdiffusion using a process modeling program developed at Stanford University [10]. The model was calibrated using diffusion data from the literature. Some of the samples were capped with a layer of CdTe prior to annealing. The capped samples were annealed in a vacuum ambient (to approximate a Te-rich boundary condition), and the uncapped samples were annealed in a Hg ambient. After annealing, the Cd profiles were measured by SIMS at Charles Evans and Associates.

3.0 RESULTS AND DISCUSSION

Examination of the SIMS data (see Figures 1-5) shows that the variation in the interdiffusion coefficient is not ideal. We used Darken's equation to extract accurate diffusion coefficients from the SIMS data. The simplest model for deviations from ideality is the regular solution model [11], which assumes that the mixing entropy is ideal and that all of the non-ideality is in the mixing enthalpy. In this model, equation 1 becomes

$$D_{MCT} = [D_{Cd}(1-x) + D_{Hg}x] \left[1 - \frac{z\Omega}{RT}(x)(1-x) \right] \quad (7)$$

where z is the coordination number (=12 for a pseudobinary zinc blende alloy), Ω is the mixing enthalpy, R is the gas constant, and T is the absolute temperature. For HgCdTe, Ω/RT has been experimentally and theoretically determined to be approximately zero [11]. The regular solution model is therefore not physically correct for the HgTe/CdTe system. Nevertheless, over a limited range in x value, it provides a simple, computationally efficient, and accurate model with which to extract the diffusion coefficients.

Equation 7 was implemented in the ALAMODE process simulator [7]. The as grown SIMS profiles were read into the simulator, along with the annealing time and temperature. ALAMODE generated 2-dimensional composition maps of the annealed structure, from which 1-dimensional composition vs. depth profiles were sliced. A value of 3.9 for Ω/RT was found to provide the most accurate fit to the experimental data. The variation in the diffusion coefficient with composition for the ideal and regular solution models is shown in Figure 7.

Examples of simulations using Equation 7 are shown in Figures 1-6. To obtain accurate diffusion coefficients, the raw SIMS data were normalized in both depth and concentration to the as-grown profiles. The simulations match the data quite closely over the composition range between 0.2 to 0.35. The close match with the data allows us to extract accurate diffusion coefficients from the SIMS profiles. Figure 8 shows a plot of D_{MCT} ($x = 0.2$) vs. temperature. At temperatures less than 350°C, samples annealed under a Hg ambient exhibited significantly more diffusion than those under a vacuum ambient. A small dependence on Hg pressure was also observed at the higher temperatures. The increase of D_{MCT} with Hg pressure implies that cation interstitials are the dominant defect in the interdiffusion process. The low-temperature data are in close agreement with those of Tang for both Hg-rich and Te-rich ambients.

The data in Figure 8 yield the following expressions for the interdiffusion coefficient:

$$\text{Hg rich, } T \leq 350 \text{ }^{\circ}\text{C:} \quad D_{cd}(\text{HgTe}) = 5.35\text{e-1} * \exp(-1.50/kT) \quad (8)$$

$$\text{Hg rich, } T > 350 \text{ }^{\circ}\text{C:} \quad D_{cd}(\text{HgTe}) = 1.99\text{e-2} * \exp(-1.33/kT) \quad (9)$$

$$\text{Te rich, } T \leq 400 \text{ }^{\circ}\text{C:} \quad D_{cd}(\text{HgTe}) = 6.40\text{e2} * \exp(-1.93/kT) \quad (10)$$

$$\text{Te rich, } T > 400 \text{ }^{\circ}\text{C:} \quad D_{cd}(\text{HgTe}) = 1.99\text{e-2} * \exp(-1.33/kT) \quad (11)$$

The same expression is used for both the Te-rich and Hg-rich ambients at higher temperatures because the data are within the experimental error. The change in activation energy and pressure

dependence between the high and low temperature regimes suggests a change in the diffusion mechanism. We believe that this is the first time that two activation energies for the interdiffusion coefficient have been reported. These activation energies will be valuable in understanding and modeling the atomic mechanisms underlying the diffusion. The strong negative deviation from ideality evidenced by the data implies that the equilibrium point defect concentrations and/or the hop activation energies are also strong functions of composition. The exact nature of these dependencies will need to be determined in order to calibrate the parameters in equations 2 - 6.

Determination of the diffusion coefficients reported in this work, extracted under well-controlled experimental conditions, is the first step toward building a comprehensive model of interdiffusion in HgTe/CdTe hetero-structures. The work needs to be expanded to other compositions and into extrinsic doping effects. Parameters that cannot be obtained from experiments, such as point defect concentrations as a function of composition, pressure, and Fermi level, must be found through an accurate *ab-initio* study of the HgCdTe system. A comprehensive model, based on the defect chemistry of this system, will lead to higher-quality, higher-performance, and lower-cost HgCdTe infrared detectors.

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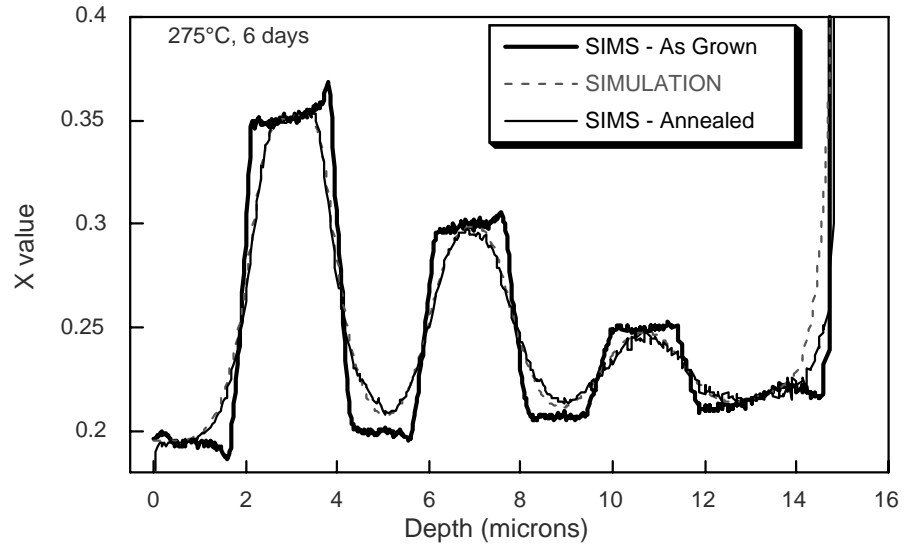


Figure 1. Experimental and simulated profiles of sample annealed at 275°C in a Hg-rich ambient.

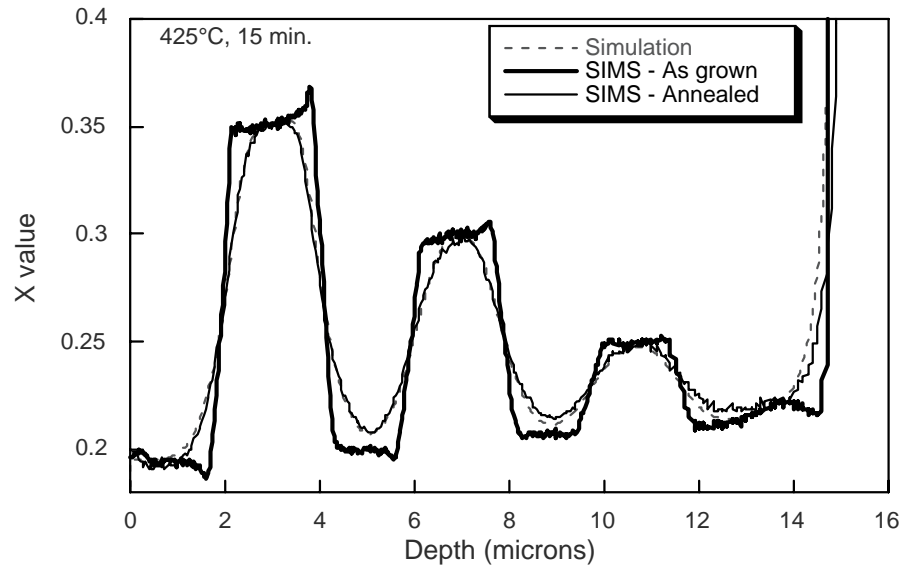


Figure 2. Experimental and simulated profiles of sample annealed at 425°C in a Hg-rich ambient.

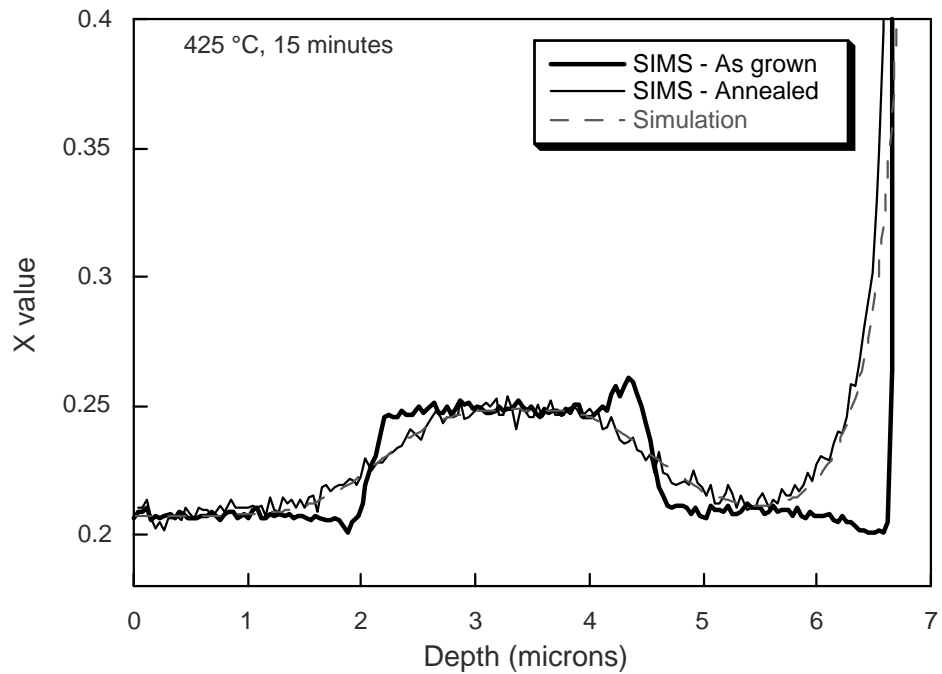


Figure 3. Same as Figure 2, except for a single variation in x value.

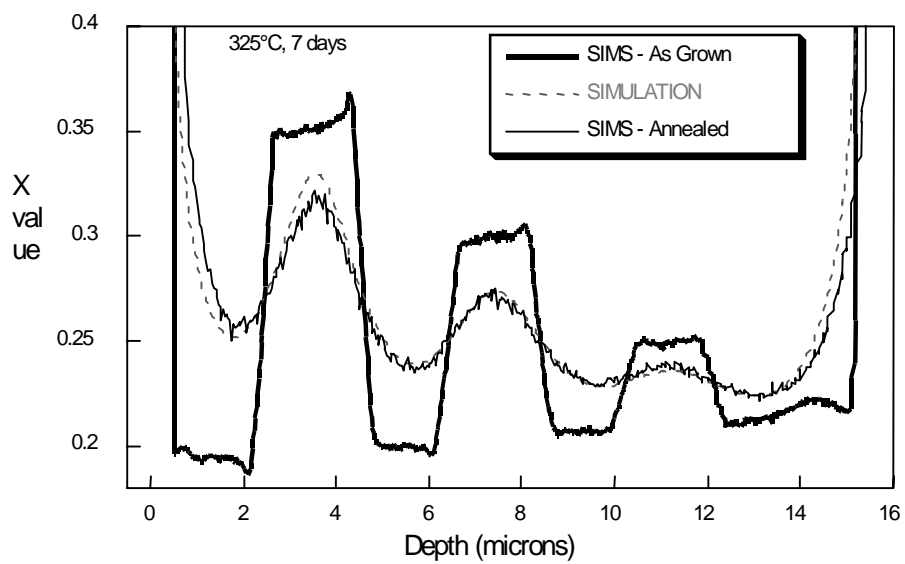


Figure 4. Experimental and simulated profiles of sample annealed at 325 °C. The sample was capped with CdTe prior to annealing.

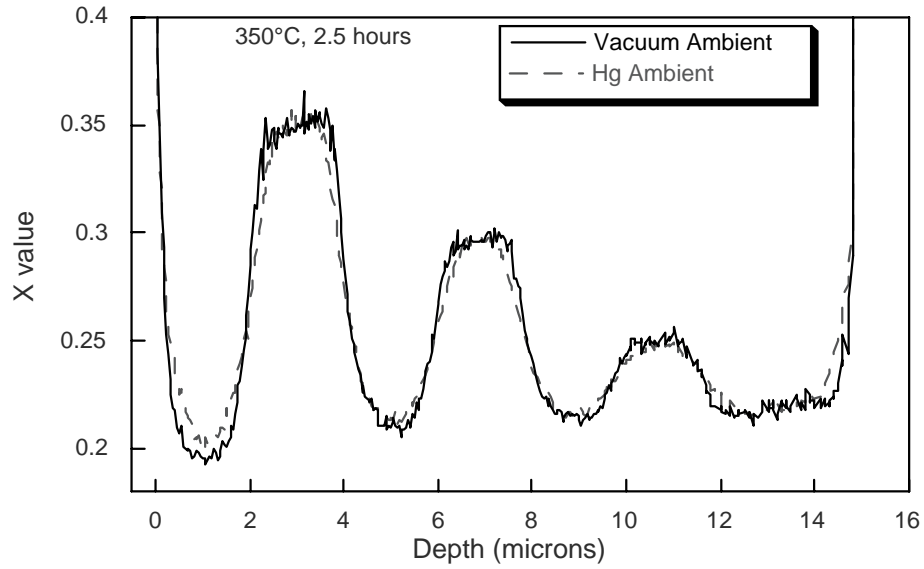


Figure 5. SIMS profiles of the Cd concentration before and after annealing in both Hg and vacuum ambients at 350 °C for 2.5 hours. Both annealed samples were capped with CdTe. The diffusivity under Hg-rich conditions is almost three times that under the vacuum ambient.

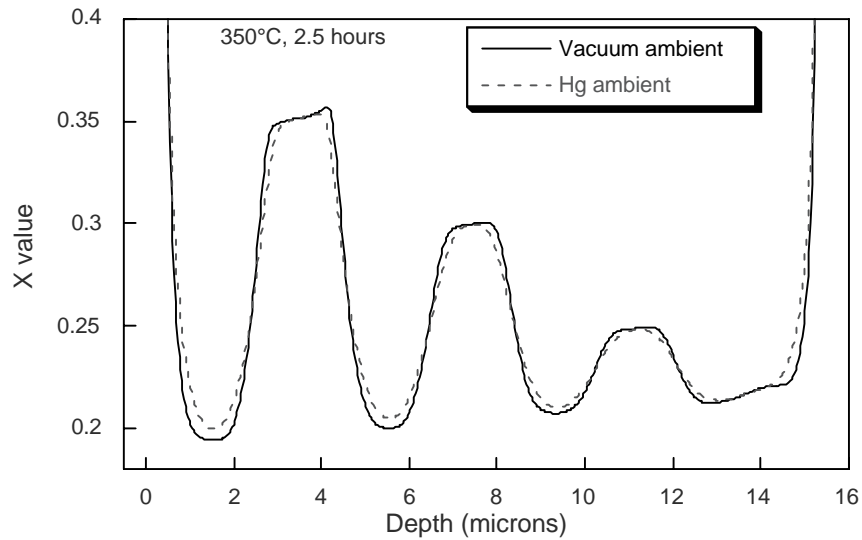


Figure 6. Comparison of simulated interdiffusion profiles annealed at 350 °C under Hg and vacuum ambients. Both samples were capped with CdTe prior to the anneal. At $x = 0.2$, the diffusivity is $1.3 \times 10^{-13} \text{ cm}^2/\text{sec}$ for the Hg ambient and $4.5 \times 10^{-14} \text{ cm}^2/\text{sec}$ for the vacuum ambient. The simulations closely match the SIMS data shown in Figure 5.

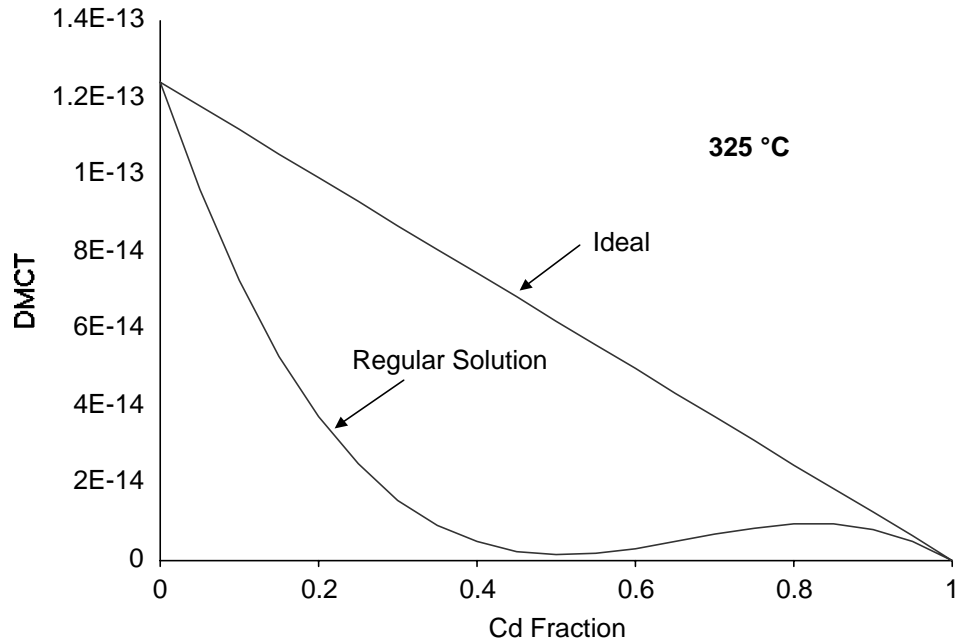


Figure 7. Comparison of ideal and regular solution models for the interdiffusion coefficient. Ω/RT equals 0 in equation 2 in the ideal model and 3.9 in the regular solution model. D_{Hg} in CdTe is $1 \times 10^{-16} \text{ cm}^2/\text{sec}$. This parameter does not affect the fits to the data if it is small. The regular solution model fits the experimental data for Cd fractions between 0 and 0.4.

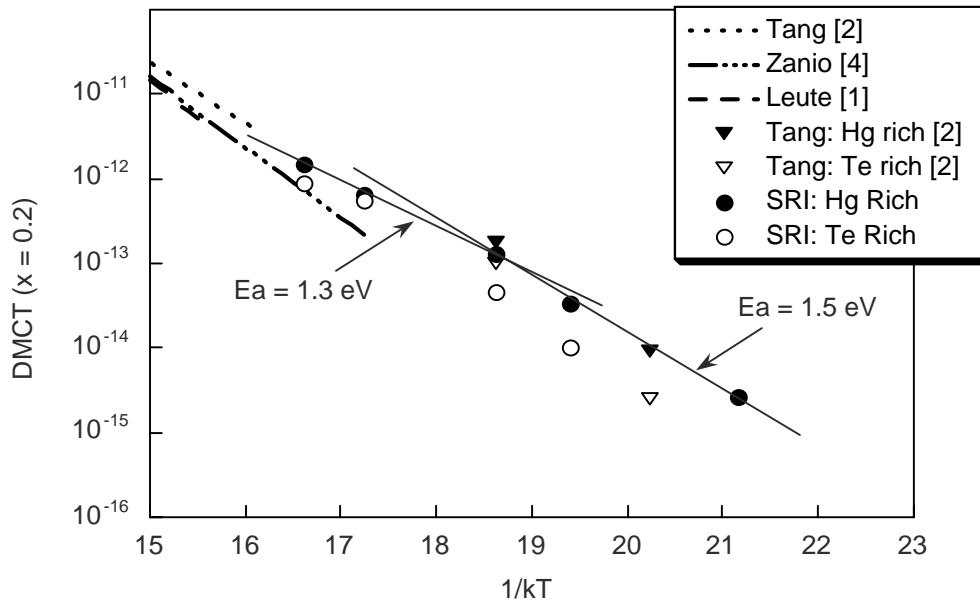


Figure 8. Comparison of the experimentally measured interdiffusion coefficient (SRI) with values from the literature. There are two branches to the data, with activation energies of 1.5 and 1.3 eV. The breakpoint is between 350 and 400 °C. At low temperatures, the experimental data are in close agreement with Tang's data.